

Chapter-13

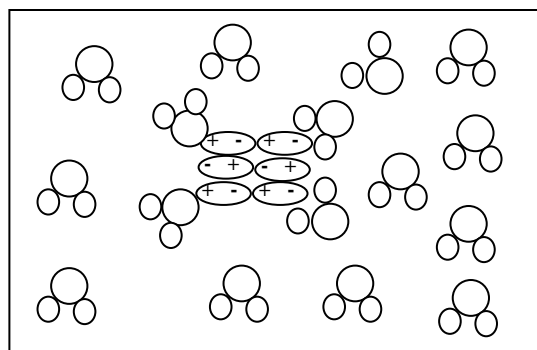
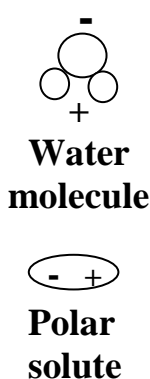
Lesson-1

I – General Properties of Aqueous Solutions (Reviewed)

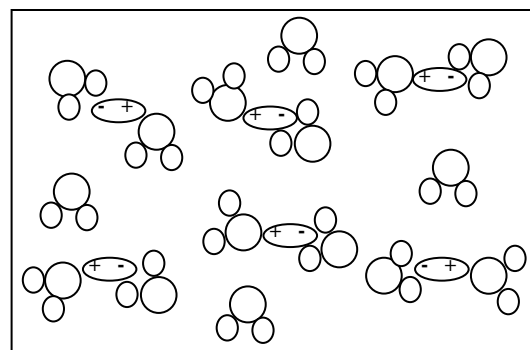
- A **solution** is a homogeneous mixture.
- A **solution** is a mixture of a **solute** that is homogeneously distributed through a **solvent**.
- In a solution, the **solute particles** are individual atoms, ions or small molecules surrounded and attracted by the solvent particles.
- In **aqueous solutions**, the solutes can be classified according to their ability to conduct an electric current through the solution.
- **Aqueous solutions** require free moving ions to conduct electricity.
- The solution process is usually **spontaneous**.

A) Nonelectrolytes:

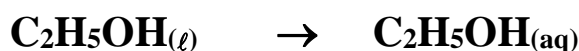
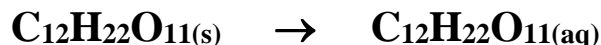
- A **nonelectrolyte** is a solute whose aqueous solution does not conduct electricity because no free moving ions are present.
- **Nonelectrolytes** are molecular substances (usually polar) that do not ionize in water.



Alcohols & Sugars

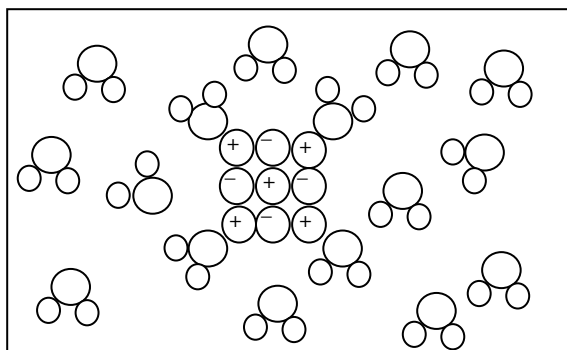
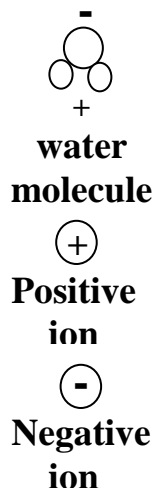


Dipole-dipole forces or hydrogen bonds are formed between the polar molecules and the polar water molecules!

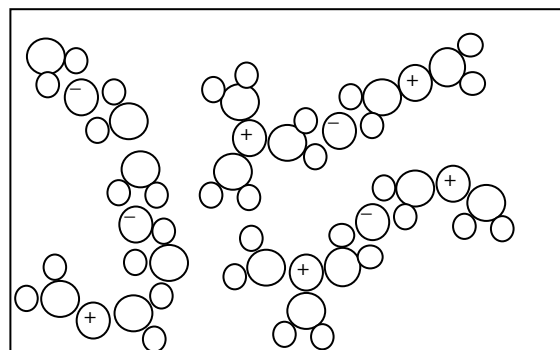


B) Electrolytes:

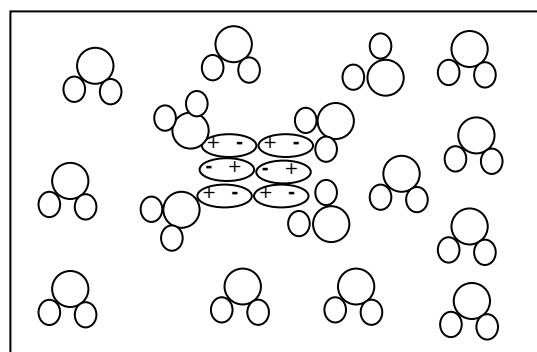
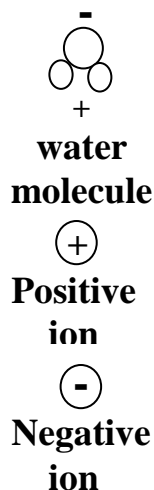
- An **electrolyte** is a solute whose aqueous solution conducts electricity.
- **Electrolytes** are ionic substances or also can be molecular substances (usually polar) that ionize in water.



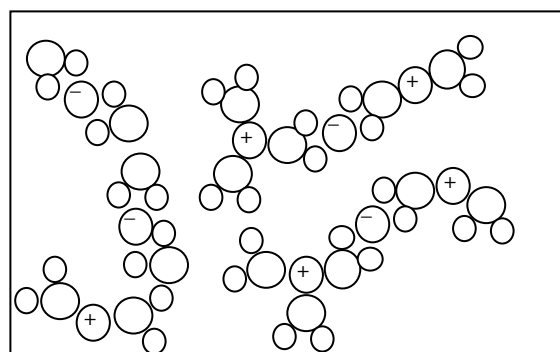
hydroxide bases & salts



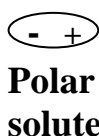
Ion-dipole forces of attraction are formed between dissolved ions and the polar water molecules!



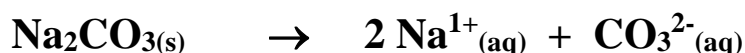
acids & organic bases



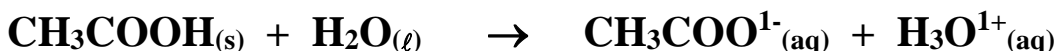
Ion-dipole forces of attraction are formed between newly created ions and the polar water molecules!



Ionic electrolytes:



Molecular electrolytes:



RNH₂ is a molecular base.

“R” can be a H atom or a “CH” group.

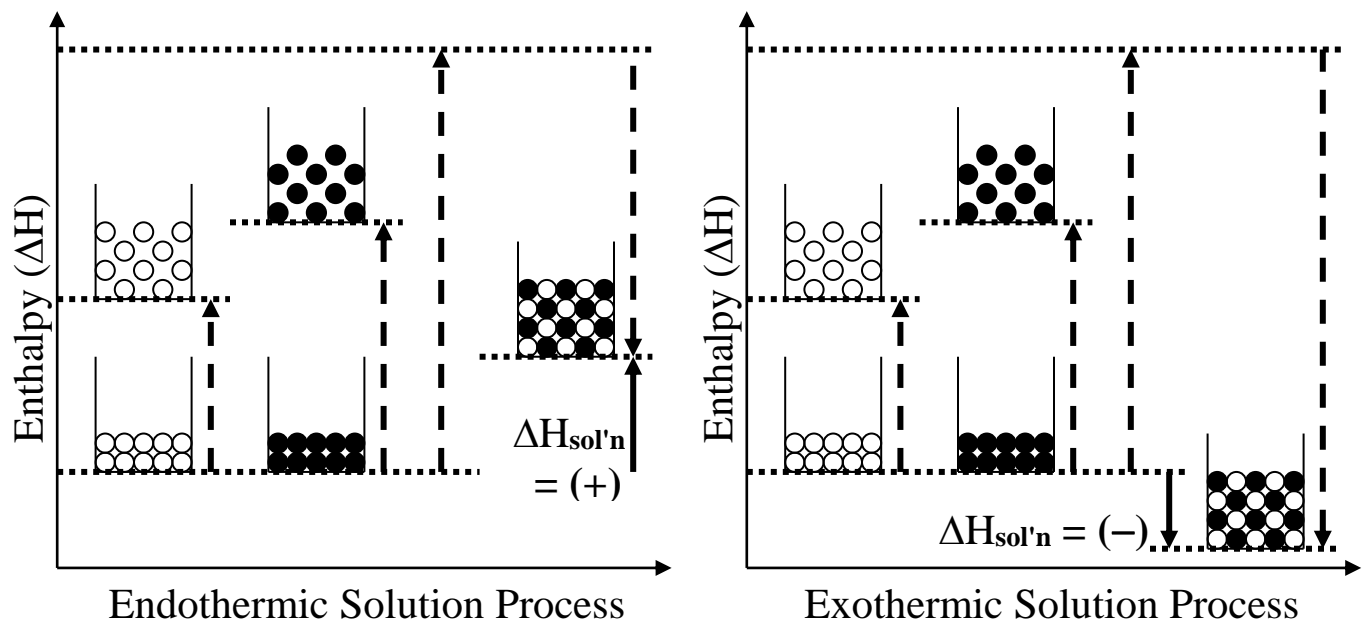
- Smaller or more highly charged ions form stronger **ion-dipole forces of attraction** with water than larger or lower charged ions.

II – The Solution Process

- The process of forming a solution can be imagined as occurring in three steps:
 - 1) The breaking of the solute-solute attractions. $\Delta H_{\text{solute}} = (+)$
 - 2) The breaking of the solvent-solvent attractions. $\Delta H_{\text{solvent}} = (+)$
 - 3) The forming of the solute-solvent attractions. $\Delta H_{\text{solution}} = (-)$
- Using Hess' law, heat of solution [$\Delta H_{\text{sol'n}}$] can be written:

$$\Delta H_{\text{solution}} = \Delta H_{\text{solute}} + \Delta H_{\text{solvent}} + \Delta H_{\text{mix}}$$

- The solution process can be **exothermic** or **endothermic**.



- Exothermic solution processes are almost always spontaneous because the solute-solvent interactions form a stable solution system because the $\Delta H_{\text{mix}} > \Delta H_{\text{solute}} + \Delta H_{\text{solvent}}$.
- However, endothermic solution processes may or may not be spontaneous.
 - ☛ If the solute-solvent interactions are too weak then the solution will be too unstable because the $\Delta H_{\text{mix}} \ll \Delta H_{\text{solute}} + \Delta H_{\text{solvent}}$. In this case the solution processes will be nonspontaneous.
 - ☛ If the solute-solvent interactions are strong enough then the solution will be stable because the $\Delta H_{\text{mix}} \lesssim \Delta H_{\text{solute}} + \Delta H_{\text{solvent}}$. In this case the solution processes will be spontaneous.

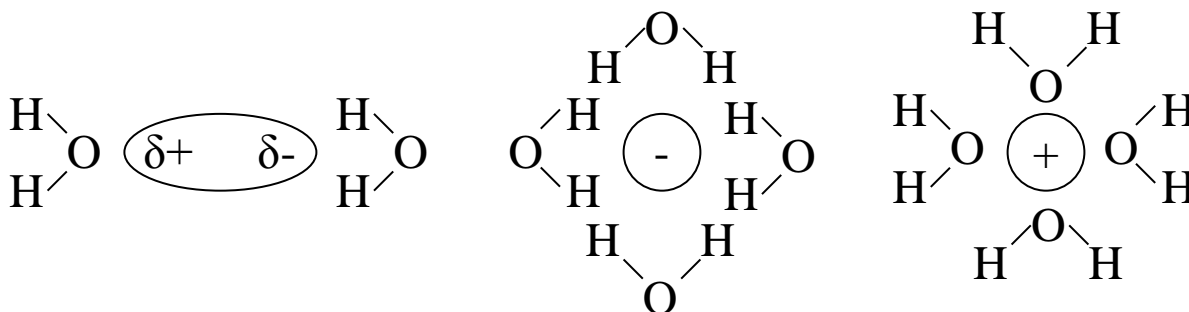
III - Factors Effecting Solubility

- A solution is **unsaturated** if more solute can be dissolved.
- A solution is **saturated** if no more solute can be dissolved.
- **Solubility** is the maximum amount of solute that can be dissolved in a set amount of solvent at a given temperature and pressure.

A) The Effect of the Solute-Solvent Interactions:

"LIKE DISSOLVES LIKE"

- **Polar solvents readily dissolve polar solutes but do not readily dissolve nonpolar solutes.**
- Water is the classic polar solvent.



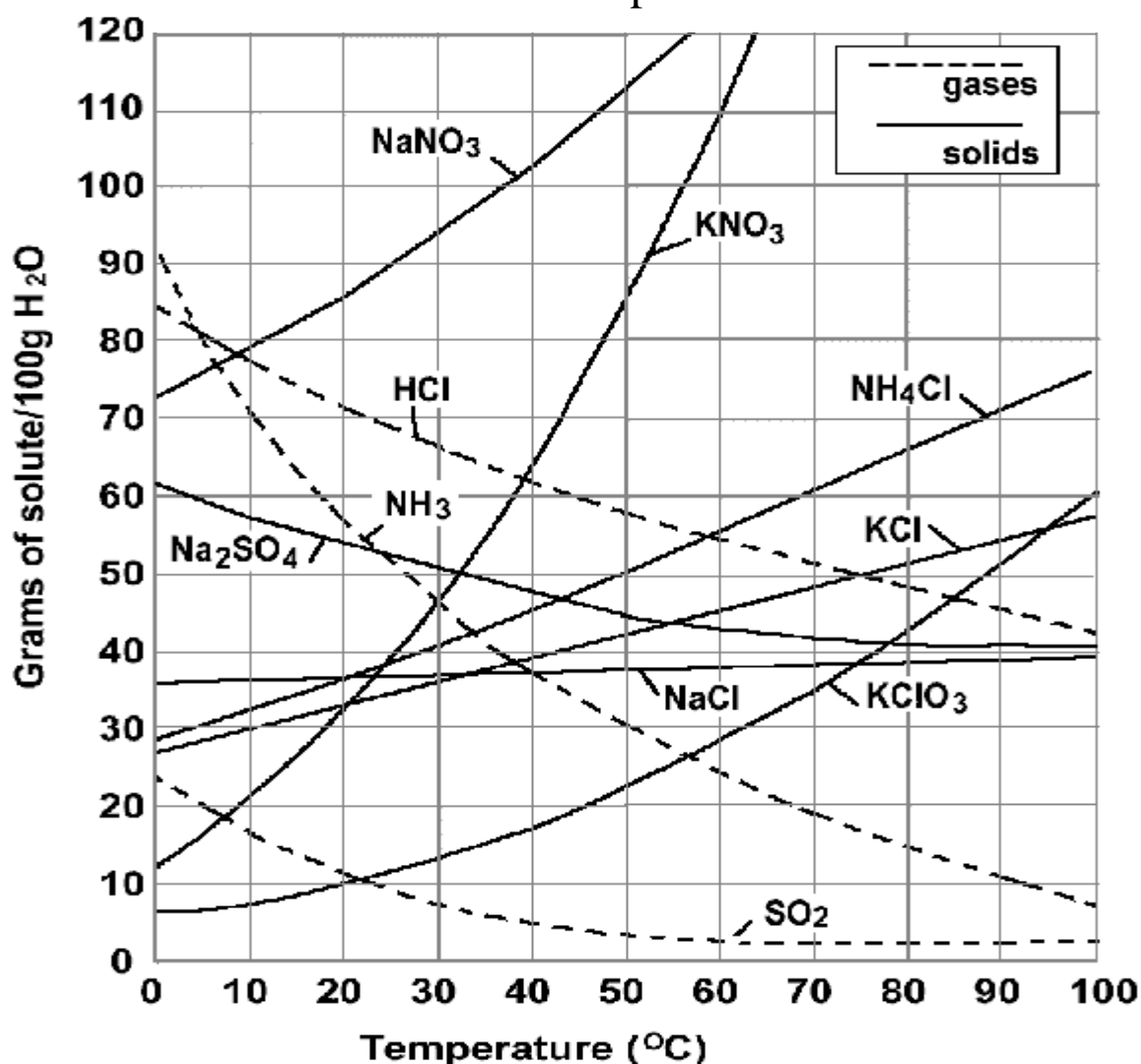
- Glycerol [$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}_2(\text{OH})$ or $\text{C}_3\text{H}_5(\text{OH})_3$], methanol [CH_3OH] and ethanol [$\text{C}_2\text{H}_5\text{OH}$] are fairly polar solvents as well.
- **Nonpolar solvents readily dissolve nonpolar solutes but do not readily dissolve polar solutes.**
- Hexane [C_6H_{12}], carbon tetrachloride [CCl_4], benzene [C_6H_6], diethyl ether [$\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$], and chloroform [CH_3Cl] are some classic nonpolar solvents.
- Acetone [CH_3COCH_3], isopropanol [$\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$]*, and pentanol [$\text{C}_5\text{H}_9\text{OH}$], are some slightly polar solvents.

Solvent	d.c.	Solvent	d.c.	Solvent	d.c.
H_2O	78.5	CH_3COCH_3	20.7	$\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$	4.3
$\text{C}_3\text{H}_5(\text{OH})_3$	42.5	* $\text{C}_3\text{H}_7\text{OH}$	18.3	C_6H_6	2.3
CH_3OH	32.6	$\text{C}_5\text{H}_9\text{OH}$	13.9	CCl_4	2.2
$\text{C}_2\text{H}_5\text{OH}$	24.3	CH_3Cl	4.8	C_6H_{12}	1.9

d.c. = dielectric constant [The larger the value the more polar the molecule.]

B) The Effect of Temperature upon the Solubility:

- An increase in temperature will favor an endothermic reaction [$\Delta H = (+)$] whereas a decrease in temperature will favor an exothermic reaction [$\Delta H = (-)$].
- Solvents at a *higher* temperature will usually be able to dissolve more **solid** or **liquid** solutes but solvents at a *lower* temperature will usually be able to dissolve more **gaseous** solutes. (See graph)
- Points below a solubility curve represent an unsaturated solution and thus more solute is able to dissolve. (See graph)
- Points on a solubility curve represent a saturated solution and thus no more solute is able to dissolve. (See graph)
- Points above the curve usually represent a saturated solution with excess undissolved solute.
- A supersaturated solution is a rare case in which more solute is dissolved than should at that temperature.

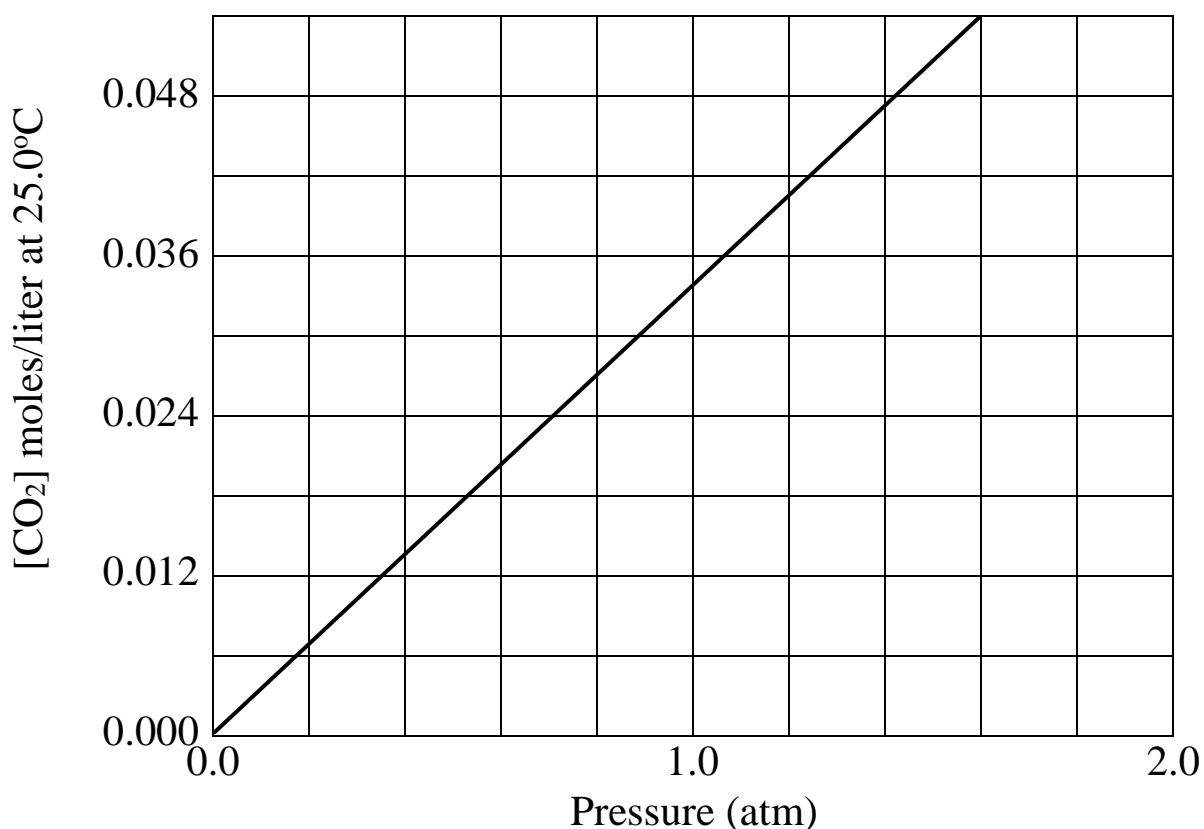


C) The Effect of Pressure upon the Solubility:

- Pressure has a negligible effect on the solubility of a solute in a solvent **except** when a gaseous solute is involved.
- The solubility of a gaseous solute in a liquid solvent is directly proportional to the gas's applied partial pressure. This is known as **Henry's law**.

$$S_g = k \times P_g \quad (\text{a "y = mx+b" equation})$$

where S_g is the gas's molar solubility, k is the gas's solubility constant, and P_g is the partial pressure of the gaseous solute over the solution. *The slope of the line on the graph below equals k .*



Q1: Based on the graph above, (i) determine the solubility constant (k) for carbon dioxide gas at 25.0°C and then the partial pressure of CO₂ needed to have a 0.15 mol/L aqueous solution at 25.0°C.

A1: (i) $m = k = \frac{0.054 - 0.00}{1.6 - 0} = 0.034 \text{ mol L}^{-1} \text{ atm}^{-1}$

(ii) $0.15 \text{ mol/L} = 0.034 \text{ mol L}^{-1} \text{ atm}^{-1} \times P_g$

$P_g = 4.4 \text{ atm}$

Q2: A filtered unsaturated solution and a filtered saturated solution both look the same. What would happen to a very small amount of solute if it were added (i) to a filtered unsaturated solution? (ii) to a filtered saturated solution?

A2: (i) The added solute would dissolve.

(ii) The added solute would not dissolve and would settle to the bottom of the container.

Q3: Polar solutes generally dissolve well in water whereas nonpolar solutes do not. Explain why, in terms of attractive forces.

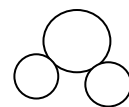
A3: Water molecules can form dipole-dipole forces and in some cases hydrogen bonds with the polar solute molecules. If these forces are more stable than the hydrogen bonding in pure water and the attractive forces in the pure polar solute, then the polar solute will dissolve well in water.

However, nonpolar solute molecules can only form weak London dispersion forces with water molecules. These attractive forces are generally less stable than the attractive forces holding the nonpolar solute molecules to each other in a pure sample and the hydrogen bonds that hold the water molecules to each in liquid water.

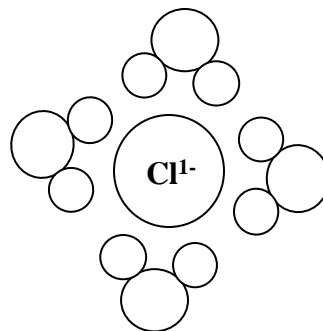
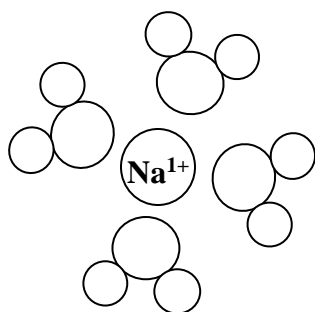
Q4: Which of these two salts, LiF or KBr, would you expect to have a higher solubility in water and why?

A4: KBr because its ions are larger than LiF's and so KBr's lattice energy would be smaller than LiF's. Salts with large lattice energies are less soluble than those with small lattice energies.

Q5: Draw a hydration sphere around each of the following ions below using four of the water molecules shown at the right around each of the two ions.



A5:



Q6: Which of these two ions, Na^{1+} or Mg^{2+} , would you expect to be more strongly hydrated in water and why?

A6: Mg^{2+} because it is ever so slightly smaller than Na^{1+} and it has twice the charge. According to Coulomb's law, the forces of attraction between the negative ends of the water molecules and the positive ions increases as the distance between them decreases and the magnitude of the charges increases.

Q7: Account for the low solubilities as well as the solubility trend of the following noble gases in water at 20°C and 1 atm gas partial pressure.

Noble Gas	Solubility (mol/L)
Ar	1.5×10^{-3}
Kr	2.8×10^{-3}
Xe	5.0×10^{-3}

A7: Noble gases are composed of nonpolar molecules which are only able to interact with water molecules via weak London dispersion forces which accounts for their low solubilities in water.

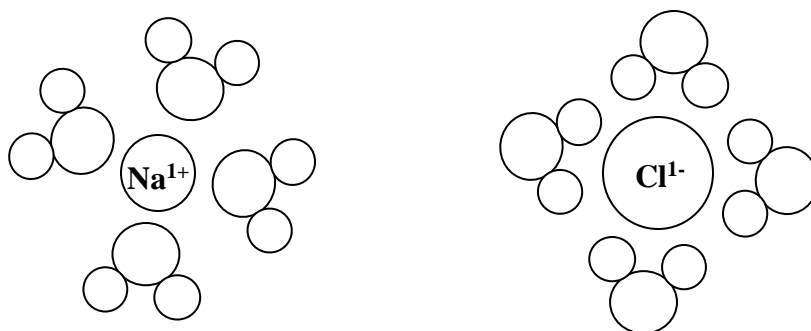
However, as the size of the nonpolar gas molecules increases (Ar to Kr to Xe) so does their polarizability. With an increasing polarizability, the strength of London dispersion forces increases, which in turn increases their solubility in water (Ar to Kr to Xe).

Chapter-13

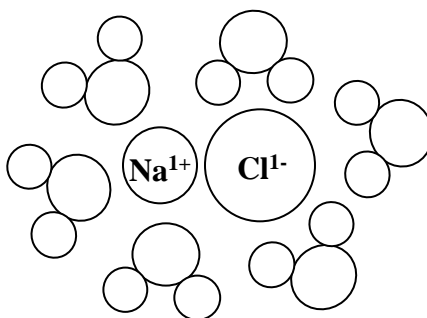
Lesson-2

IV - Expressing Solution Concentration Qualitatively

- A solution with a relatively small concentration of solute is said to be dilute.
- A solution with a relatively large concentration of solute is said to be concentrated.
- The ions in a dilute aqueous solution of an ionic solute behave differently from the ions in a concentrated aqueous solution of an ionic solute.
- In a dilute aqueous solution of an ionic solute, the ions behave as one would expect. The positive and negative ions are completely separated and individually hydrated by water molecules.



- In a concentrated aqueous solution of an ionic solute, some of the positive and negative ions become “stuck to each other” and as such become hydrated by water molecules as an ion-pair.



- The degree of ion-pairing increases as (i) the solution becomes more and more concentrated and (ii) with greater ionic charges. (At the same concentration, MgSO_4 exhibits a greater degree of ion-pairing than NaCl .)

V - Expressing Solution Concentration Quantitatively

A) Molarity (M): (Reviewed)

$$M = \frac{\text{moles solute}}{\text{liters solution}}$$

Q1: What would be the molarity of glucose in a 101.5 mL solution that has 50.0 g of glucose dissolved in it?

$$\text{A1: } 50.0 \text{ g C}_6\text{H}_{12}\text{O}_6 \times \frac{1 \text{ mole}}{180. \text{ g}} = 0.278 \text{ mol}$$

$$M_{\text{glucose}} = \frac{0.278 \text{ mol}}{0.1015 \text{ L}}$$

$$M_{\text{glucose}} = 2.74 \text{ M or } 2.74 \text{ molar}$$

Q2: If a saturated solution of NaCl at 20°C has a concentration of 5.98 mol/L, then how many grams of NaCl would be present in a 255 mL saturated solution?

$$\text{A2: } 5.98 \frac{\text{mol}}{\text{L}} \times 0.255 \text{ L} \times \frac{58.5 \text{ g}}{1 \text{ mol}} = 89.2 \text{ g NaCl}$$

Q3: What is the molarity of chloride ions in a solution that is formed by mixing 25 mL of 0.40 M NaCl with 75 mL of 0.60 M MgCl₂?

$$\text{A3: } 0.40 \frac{\text{mol}}{\text{L}} \text{ NaCl} \times 0.025 \text{ L} \times \frac{1 \text{ mol Cl}^{1-}}{1 \text{ mol NaCl}} = 0.010 \text{ mol Cl}^{1-}$$

$$0.60 \frac{\text{mol}}{\text{L}} \text{ MgCl}_2 \times 0.075 \text{ L} \times \frac{2 \text{ mol Cl}^{1-}}{1 \text{ mol MgCl}_2} = 0.090 \text{ mol Cl}^{1-}$$

$$0.100 \text{ mol Cl}^{1-} \times \frac{1}{0.100 \text{ L}} = 1.00 \text{ M Cl}^{1-}$$

B) Diluting of a Solution of Known Molarity: (Reviewed)

$$M_{\text{conc}} \bullet V_{\text{conc}} = M_{\text{dilute}} \bullet V_{\text{dilute}}$$

Q4: What would be the molar concentration of a solution of glucose if 50.0 ml of a 2.74 M glucose solution were diluted to 250.0 ml with distilled water?

A4: $(2.74)(50.0) = (X)(250.0)$

$$X = 0.548 \text{ M}$$

C) Preparing Solutions of Known Molarity: (Reviewed)

Q5: Describe how would you prepare a 100.0 mL of a 0.150 M solution of NaCl from a 1.00 M stock solution?

A5: $(1.00)(X) = (0.150)(100.0)$

$$X = 15.0 \text{ mL}$$

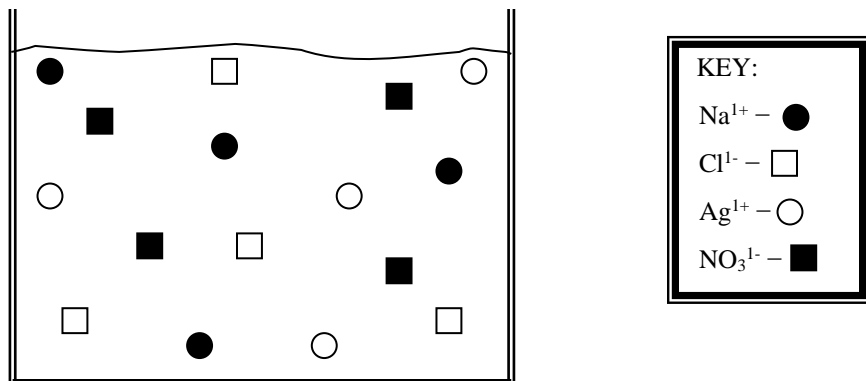
- *Half fill a 100-milliliter volumetric flask with water.*
- *Pipette in 15.0 mL of the 1.00 M stock solution of NaCl.*
- *Gently swirl.*
- *Add water to the flask's 100.0 calibration mark.*
- *Stopper the volumetric flask and invert to mix.*

Q6: Describe how would you prepare a 100.0 mL of a 0.150 M solution of NaCl from solid NaCl?

A6: $0.150 \frac{\text{mol}}{\text{L}} \text{ NaCl} \times 0.100 \text{ L} \times \frac{58.5 \text{ g NaCl}}{1 \text{ mol}} = 0.878 \text{ g NaCl}$

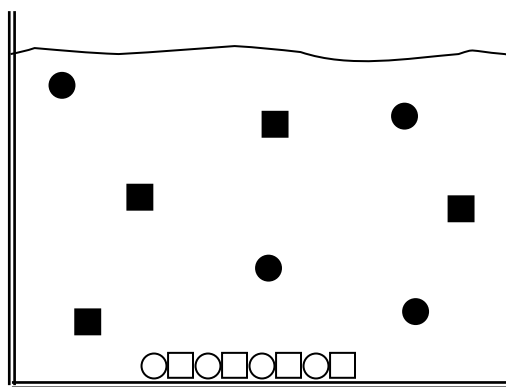
- *Add 0.878 g NaCl to a 100-mL volumetric flask.*
- *Half fill a 100-milliliter volumetric flask with water.*
- *Gently swirl.*
- *Add water to the flask's 100.0 calibration mark.*
- *Stopper the volumetric flask and invert to mix.*

Q7: An aqueous solution of NaCl and an aqueous solution AgNO₃ are poured into a beaker. The particle diagram below shows the contents of the beaker the very moment the two solutions were added and before any potential reaction has taken place. (Water molecules have not been shown in order to simplify the particle diagram.)



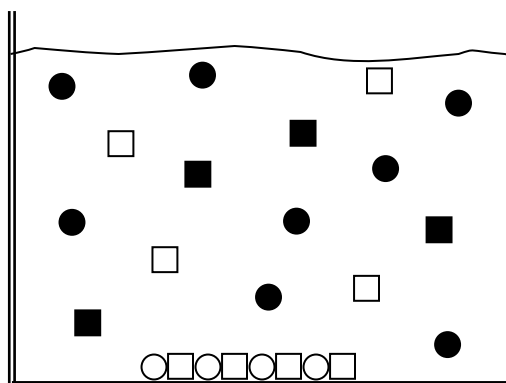
Using the key above, draw a particle diagram to show the contents of the beaker after a period of time has elapsed.

A7:

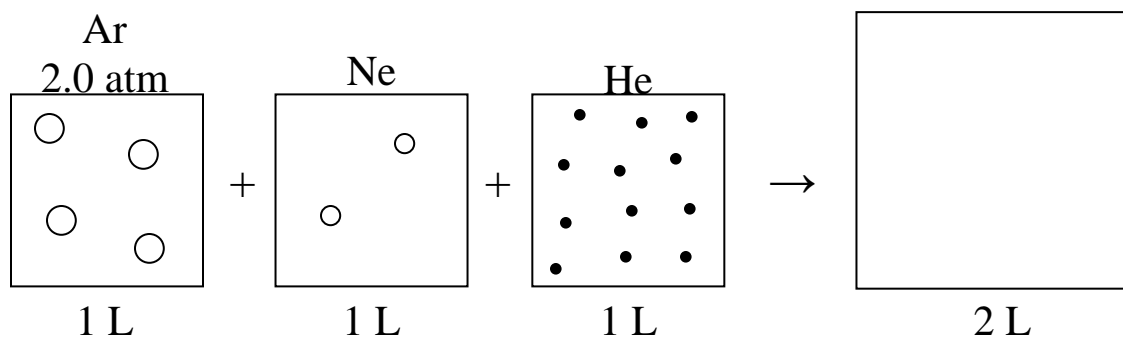


Q8: A student repeats the activity in question-7. However, the aqueous NaCl solution is twice the original concentration. Draw a particle diagram to show the contents of the beaker after a period of time has elapsed.

A8:



Q9: A mixture of gases is a solution since they mix homogeneously.



The figure above represents three sealed 1.0 L vessels, each containing a different noble gas at 298 K. The pressure of Ar in the first vessel is 2.0 atm. After all the gases are combined in a previously evacuated 2.0 L vessel, what is the total pressure of the solution of gases at 298 K?

A9: Since 4 Ar particles has a pressure of 2.0 atm in a 1 L vessel at 298 K, then 2 particles of Ne gas will have a pressure of 1.0 atm in a 1 L vessel at 298 K, and 12 particles of He gas will have a pressure of 6.0 atm in a 1 L vessel at 298 K. Mixed together in a 1 L vessel, the gases would have a total pressure of 9.0 atm. Thus in a 2 L vessel, the gases would have a total pressure of ...

4.5 atm.

Q10: Using information from question-9, calculate the molarity of the argon gas in the 2 L vessel at 298 K.

A10: $PV = nRT$

$$(2.0 \text{ atm})(1.0 \text{ L}) = n(0.08206 \text{ atm}\cdot\text{L/mol}\cdot\text{K})(298 \text{ K})$$

$$n = \underline{0.082 \text{ mol Ar}}$$

$$M = \frac{0.082 \text{ mol Ar}}{2.0 \text{ L}}$$

$$M = \underline{0.041 \text{ M Ar}}$$

Q11: When the average person exhales, the CO₂ concentration in the expired air mixture rises to a peak of 4.6% by volume.
 (i) Determine the partial pressure of the CO₂ in the expired air at its peak, assuming 1.00 atm pressure and 37.0°C body temperature. (ii) Determine the molarity of the in the expired air at its peak, assuming 37.0°C body temperature

A11: (i)
$$\frac{P_{\text{CO}_2}}{V_{\text{CO}_2}} = \frac{P_{\text{air}}}{V_{\text{air}}}$$

$$\frac{P_{\text{CO}_2}}{4.6\text{L}} = \frac{1.00\text{ atm}}{100\text{L}}$$

$$P_{\text{CO}_2} = 0.046\text{ atm}$$

(ii)
$$\frac{n}{V} = \frac{P}{RT}$$

$$M = \frac{P}{RT}$$

$$M = \frac{0.046\text{ atm}}{(0.08206\text{ atm}\cdot\text{L}/\text{mol}\cdot\text{K})(310.0\text{ K})}$$

$$M = 0.0018\text{ mol/L}$$

Q12: Two liquids are **miscible** if they mix together in all proportions.
 (i) Would you expect glycerol – CH₂(OH)CH(OH)CH₂(OH) – to be miscible in each other and why or why not? (ii) Which of the following attractive forces are able to exist between a water molecule and a glycerol molecule? *Dipole-dipole forces, London dispersion forces, ion-dipole forces, hydrogen bonding.*

A12: (i) Glycerol and water should mix together in all proportions. The three hydroxyl (–OH) groups on the glycerol should allow for very strong hydrogen bonding with water creating a stable mixture. (ii) Hydrogen bonding, dipole-dipole forces, and London dispersion forces.